

RESEARCH PAPER RP1351

Part of *Journal of Research of the National Bureau of Standards*, Volume 25,
December 1940

PREPARATION OF BENZOIC ACID OF HIGH PURITY

By Frank W. Schwab and Edward Wichers

ABSTRACT

A comparative study was made of methods for preparing benzoic acid of a purity not less than 99.99 mole percent. The methods studied were fractional distillation in vacuum, recrystallization from water and from purified benzene, fractional freezing, oxidation of purified toluene with subsequent recrystallization from water, and hydrolysis of purified benzoyl chloride. The best preparations were obtained by repeated crystallization from benzene, by hydrolysis of benzoyl chloride, and by fractional freezing. They had a purity of 99.999 mole percent as determined by the freezing range and by specific heat measurements. The freezing point of benzoic acid is tentatively given as $122.36 \pm 0.01^\circ \text{C}$.

CONTENTS

	Page
I. Introduction.....	747
II. Criteria of purity.....	748
1. Vaporizing and condensing behavior.....	748
2. Crystallizing and melting behavior.....	749
III. Stability of benzoic acid.....	750
IV. Methods of preparation.....	752
1. From parent substances by selected reactions.....	752
(a) Oxidation of toluene.....	752
(b) Hydrolysis of purified benzoyl chloride.....	752
2. By purification of a commercial product.....	752
(a) Distillation.....	752
(b) Fractional freezing.....	753
(c) Crystallization from solvents.....	753
V. Results and discussion.....	756

I. INTRODUCTION

Many properties of substances are determined by comparative rather than by absolute methods. The accuracy of comparative methods depends on the precision of the measurements and on the accuracy with which the properties of the standard substance used for comparison are known. As methods of making comparative measurements improve, an increasing demand is made on the accuracy with which the properties of the standard substance are determined. A high degree of accuracy in the original determination of the properties of this reference substance requires not only a high degree of uniformity of composition but also a close approach to ideal purity.

Benzoic acid is commonly used as a standard substance for calorimetry and acidimetry, and "standard samples" of this substance have been issued by the National Bureau of Standards for many years. Morey¹ made a study of the suitability of benzoic acid as a primary standard in acidimetry and alkalimetry. He found that it could be titrated with a standard alkali to a high degree of accuracy

¹ George W. Morey, *J. Am. Chem. Soc.* **34**, 1027 (1912).

and that this method afforded a rapid and accurate means of comparing the purity of various preparations. Morey purified commercial benzoic acid by recrystallizing it from solvents and fractionally subliming it in a vacuum.² Weaver³ purified the acid in a manner similar to that used by Morey. Each fused the acid prior to titration. This treatment was designed to remove water that was absorbed during contact with air.

When a redetermination of the heat of combustion of benzoic acid was recently undertaken by the Heat Measurements Section of this Bureau, with an anticipated precision of 0.01 percent, it became desirable to prepare benzoic acid which would have a purity of at least 99.99 mole percent.

II. CRITERIA OF PURITY

Criteria of purity for a nearly pure organic substance should be independent of known properties of the substance. Physical properties are usually not known with sufficient accuracy to permit estimation of purity by comparison even though the identities of the compounds under consideration and of some of the impurities in it are known. Independent criteria which are generally used depend on (1) vaporizing or condensing behavior and (2) freezing or melting behavior. If, like benzoic acid, the substance is a moderately strong acid, its acid value is also a useful index of purity and is often so used. The acidimetric method as commonly applied is not suitable, however, for determining differences in purity smaller than 0.01 percent.

1. VAPORIZING AND CONDENSING BEHAVIOR

The behavior on evaporation or condensation as a criterion of purity⁴ is suitable only for substances that do not decompose significantly, and is generally utilized by measuring the boiling range under constant pressure or by determining the initial and final vapor pressures during an isothermal vaporization or condensation. The method is most sensitive when the substance is distilled in an efficient fractionating column. The boiling points under the same external pressure, or the difference in vapor pressure at the same temperature, of the first and last fractions may then be compared.

It is known that benzoic acid undergoes measurable decomposition at temperatures 50° to 100° C below its normal boiling point (about 250° C). The identity of some of the products of decomposition is not known, but in the course of the present work it was found that one of the reactions at these temperatures is the slow formation of benzoic anhydride and water. Although the concentrations of anhydride and of water are probably small under equilibrium conditions at 130° C or somewhat higher temperatures, transformation of the acid to these products is rapid enough so that distillation in an efficient fractionating column for the desired separation is not practicable. It is obvious, therefore, that this method cannot be readily applied under conditions most suitable for obtaining the highest sensitivity.

² George W. Morey, *J. Am. Chem. Soc.* **34**, 550 (1912).

³ E. R. Weaver, *J. Am. Chem. Soc.* **35**, 1309 (1913).

⁴ E. W. Washburn, *The problem of establishing the identity and purity of a hydrocarbon obtained from petroleum*, *J. Ind. Eng. Chem.* **22**, 985 (1930). Also see Martin Shepherd, *A critical test for the purity of gases*, *BS J. Research* **12**, 185 (1934) RP 643. For a further discussion of this subject see W. Świątosiński, *Ebulliometry* (Chemical Publishing Co., New York, N. Y., 1937).

2. CRYSTALLIZING AND MELTING BEHAVIOR

In the work described in this paper the purity of benzoic acid was determined from its behavior during freezing or melting. The test based on the freezing behavior is customarily applied by determining the cooling curve through the entire freezing range. White⁵ has discussed the theoretical aspects of this method and the assumptions involved.

In adapting this method to the present problem, the authors⁶ found numerous sources of error which limited its accuracy but which could be largely eliminated by comparing the freezing range of the substance with that of the same substance after adding a known concentration of a properly chosen "impurity." By so doing it was found possible to use any selected interval of the freezing range and, with appropriately refined technique, to determine concentrations of impurity of 0.01 mole percent or less. Since the completion of the work just cited, the technique has been further perfected.⁷ It was found that for preparations containing up to about 0.30 mole percent of impurity the uncertainty of the determination is not greater than 0.01 mole percent. The purity of highly pure samples was determined to 0.001 mole percent or better by making several observations on a given preparation. It was possible, for example, to distinguish between two preparations estimated, respectively, as 99.999₂ and 99.999₄ mole percent pure. The accuracy of the method is limited in part by the very slow formation of benzoic anhydride when the liquid to be frozen is thoroughly dried.

Another sensitive test of purity is based on the variation in the heat capacity of a substance at temperatures slightly below its melting point. This test involves a determination of the first part of the melting range by calorimetric rather than by thermometric means. Any departure from a linear variation of heat capacity with respect to temperature is ascribed to absorption of heat associated with melting. Several of the preparations described in this paper were so examined by R. S. Jessup, of the Heat Measurements Section of this Bureau, in accordance with a procedure described by Dickinson and Osborne.⁸

It will be noted from table 2 that the estimates of purity of several preparations which are based on the calorimetric method are in close agreement with those based on the measurement of the freezing range. The samples used for the calorimetric measurements were prepared before the slow formation of benzoic anhydride during drying had been observed. It is possible, therefore, that some of these samples were somewhat "overdried" and hence less pure than the corresponding ones used later for the measurement of the freezing ranges. The calorimetric method, although inherently more sensitive than the thermometric method is more time-consuming.

⁵ Walter P. White, *J. Phys. Chem.* **24**, 393 (1920).

⁶ F. W. Schwab and Edward Wichers, *Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance*. This paper appears as a chapter in *Temperature, Its Measurement and Control in Science and Industry*, (Reinhold Publishing Co., New York, N. Y., 1940).

⁷ All the results reported in this paper were obtained by freezing the substance at twice the initial rate employed in the earlier work. This was done by doubling the difference in temperature between the freezing substance and the cooling bath. The desired part of the freezing range was observed in about 60 minutes, and better conditions were obtained at the beginning of freezing.

⁸ H. C. Dickinson and N. S. Osborne, *Bul. BS* **12**, 49 (1915) S248. See also Evald L. Skau, *J. chim. phys.* **31**, 366 (1934), for a quantitative treatment of this subject.

In the remainder of this paper all references to "purity" and "content of impurity" are based on determinations of the freezing range.

III. STABILITY OF BENZOIC ACID

Before it was possible to reach a conclusion as to the relative merits of various methods of purification, and of various tests of purity, it was necessary to investigate the stability of benzoic acid at temperatures above its melting point. Three samples of material currently issued by the Bureau as Standard Sample 39e (containing 0.017 mole percent of impurity) were heated in sealed glass tubes (Pyrex) at 200° C for 72 hours. One was filled with air and a second with oxygen, each under a pressure of 1 atmosphere, and a third was evacuated. After this treatment the first contained 0.046; the second, 0.047; and the third, 0.025 mole percent of impurity, as estimated from the freezing behavior. The color of the sample heated in the evacuated tube was pale yellow; that of the sample heated under air, light brown; and that of the sample heated under oxygen, slightly darker brown. From these results it appears that of the slight amount of decomposition which occurs below 200° C more is to be attributed to oxidation than to dissociation of the acid into benzoic anhydride and water.

It was concluded that any treatment of the acid involving heating at temperatures not over 135° C for relatively short periods was not likely to cause significant deterioration. More exact information about the formation of anhydride was obtained in another way. During the process of repeatedly measuring the freezing range of a very pure sample of benzoic acid, the acid was dried before freezing and stirred while freezing by passing through it air which had been dried by phosphorus pentoxide. The dried air was passed at a constant rate through the molten benzoic acid, which was maintained at a temperature of about 130° C, for measured intervals between successive freezings. A progressive but slow decrease in purity was observed. After freezing the sample five times, the total change was 0.005 mole percent. Since benzoic anhydride is a possible product of this treatment, it seemed reasonable that an increase in the partial pressure of the water in the air would reverse the reaction. It was found that a partial pressure of water in the air equal to 0.5 mm Hg (corresponding to 0.005 mole percent dissolved in the acid)⁹ was sufficient to do this, and by this treatment the content of impurity was reduced from 0.005 to 0.001 mole percent.

In another series of experiments a known quantity of benzoic anhydride (0.764 mole percent) was added to the benzoic acid. The concentration of water in the liquid acid was controlled by passing through it air saturated with water at selected temperatures. The rate of hydrolysis at 130° C was measured by maintaining a known concentration of water during a measured interval of time, then removing the excess of water from the liquid by passing through it air

⁹ The relation between the amount of water dissolved in benzoic acid and the partial pressure of the depression of the freezing point of the acid is in equilibrium was determined approximately by observing the depression of the freezing point of the acid when frozen successively in equilibrium with dry air and with air containing 4.6 and 17.8 mm of water vapor. The indicated partial pressures of water were established by saturating air with water at 0° C and at 20.0° to 20.3° C, respectively. At these partial pressures the observed depressions of the freezing temperature were 0.04° and 0.15° C, which correspond to 0.05 and 0.20 mole percent of dissolved water.

dried over phosphorus pentoxide and observing the change in freezing temperature. The results in table 1 show that the reaction may be represented by the equation

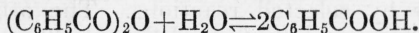


TABLE 1.—Rate of hydrolysis of benzoic anhydride

[Temperature=130° C]

Minutes	Mole per- cent of a	Mole per- cent of x	$a-x$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$	k
Concentration of water = 0.31 mole percent						
390	0.73	0.27	0.46	1.6	0.1959	0.0012
240	.46	.17	.30	1.6	.1931	.0019
180	.30	.05	.24	1.2	.0864	.0011
120	.24	.04	.21	1.2	.0756	.0015
300	.18	.06	.12	1.5	.1614	.0012
Concentration of water = 0.05 mole percent						
165	0.21	0.02	0.19	1.1	0.0374	0.0005
180	.19	.01	.18	1.1	.0253	.0003

Since the concentration of water is held constant and the rate of the reverse reaction is negligible in comparison with the rate of hydrolysis, the reaction is of the first order. The velocity constant for this reaction, for a given concentration of water in the liquid, may be calculated from the equation

$$k = \frac{1}{t} \ln \frac{a}{a-x},$$

in which

- a = mole percent of benzoic anhydride at the beginning,
 x = mole percent of benzoic anhydride changed to resultants,
 t = time in minutes,
 k = velocity constant.

No attempt was made to measure the rate of hydrolysis accurately. However, the results show that the rate of reaction is dependent on the concentrations of water and of anhydride. After the last observation 0.18 mole percent of anhydride remained. Several milliliters of water was then added to the acid, and the mixture again heated to 130° C. The excess water was removed by washing with dry air. After this treatment, the purity of the acid was 99.996 mole percent, which indicates that substantially complete hydrolysis of the anhydride had taken place. Since the acid was kept at about 130° C for 50 hours before and 30 hours during this course of treatment, its final purity shows that, except for the formation of anhydride, benzoic acid is remarkably stable at temperatures not much above its melting point. As previously noted, the formation of the anhydride occurs only when the acid is in contact with very dry air.

IV. METHODS OF PREPARATION

Two general courses were followed in the preparation of pure benzoic acid. One was to prepare the acid from carefully purified parent substances by selected reactions. The other was to start with a relatively pure acid (Standard Sample 39e) and purify it by the best available processes.

1. FROM PARENT SUBSTANCES BY SELECTED REACTIONS

(a) OXIDATION OF TOLUENE

One of the reactions chosen was the oxidation of toluene which had been purified by distillation until its boiling point was constant to within 0.01°C . This was done to insure the elimination of impurities, such as xylenes, which would yield derivatives difficult to separate from the benzoic acid. The toluene was treated with potassium permanganate in a nearly neutral solution. The partial oxidation of organic substances is difficult to control, and in the oxidation of toluene evidence was obtained of the formation of aliphatic acids and also of some tarry material. After four crystallizations from water the product was 99.980 mole percent pure. It was, therefore, less pure than Standard Sample 39e (99.983 mole percent). Because of these difficulties this method was abandoned as a means of providing benzoic acid of high purity, although some modification of the procedure might have yielded a better product.

(b) HYDROLYSIS OF PURIFIED BENZOYL CHLORIDE

A reaction which proved to yield highly pure benzoic acid was the hydrolysis of carefully distilled benzoyl chloride.¹⁰ Two lots of benzoyl chloride were used in this work. A portion of lot 1 was hydrolyzed in the vapor phase at about 100°C . Benzoyl chloride was brought into the reaction chamber by passing a stream of nitrogen through the liquid at the desired rate. An excess of water vapor was simultaneously passed into the reaction chamber, which served to continuously wash benzoic acid from it and thus to minimize the possibility of secondary reactions. Hydrolysis of a second portion of lot 1, in the liquid phase, proceeded very rapidly when the substance was treated with an excess of water and heated to about 115°C . Each product was crystallized seven times from water. The purity of each was 99.996 mole percent. Since vapor-phase hydrolysis is slow and since there was no measurable difference in the purity of the products obtained, a portion of benzoyl chloride from lot 2 was hydrolyzed in the liquid phase. The product was not recrystallized from water; hydrogen chloride and water were removed by passing dry air through the liquid. The product so obtained was 99.999 mole percent pure.

2. BY PURIFICATION OF A COMMERCIAL PRODUCT

(a) DISTILLATION

An unsuccessful attempt was made to purify Standard Sample 39e by fractional distillation in an evacuated bulb in which the distillate collected as liquid (at about 123°C). One-fifth of the distillate was

¹⁰ Commercial benzoyl chloride was distilled under the supervision of F. D. Rossini. The substance was twice distilled in a 30-plate bubble-cap still under 215-mm pressure to minimize the possibility of thermal decomposition. The still was charged twice with 2,500 ml of benzoyl chloride, and each time about 1,200 ml was collected as the middle fraction. The combined middle portions, lot 1, were redistilled and about 1,500 ml collected, rejecting about equal quantities of the first and last fractions. This 1,500 ml (lot 2) distilled at about 150°C , with a range not greater than 0.2°C , the limit of sensitivity of the thermometer.

then distilled into a second receiver in the same way. A comparison of the freezing ranges of these three fractions showed no improvement in purity in the middle fraction and a slight decrease in the end fractions. Evidently the impurities in the original material did not differ enough in vapor pressure from benzoic acid to be removable by a simple process of distillation. In view of the difficulties of operating an efficient rectifying column at low pressures, above the melting point of the acid (122.4°C), this method was abandoned.

E. R. Weaver of this Bureau has suggested that sublimation in a partial vacuum would be more successful than distillation, provided the temperature of condensation (in the solid phase) were properly regulated and the vapor space ventilated so that the vapor phase would never become saturated with any of the impurities. In view of the success of other methods of purification this procedure was not tried.

(b) FRACTIONAL FREEZING

Fractional crystallization can be accomplished either with or without the use of a solvent. The latter method, fractional freezing, was suggested by the use of the freezing range as a criterion of purity. This method was first applied by allowing the molten acid to freeze rather slowly in a Dewar flask (method 1). Solid and liquid were kept thoroughly mixed. When the substance was one-half to two-thirds frozen, the remaining liquid was drawn off by suction. The solid portion was then remelted and the process repeated. The increase in purity which resulted from the use of this method was somewhat slower than was expected. This indicated that a satisfactory approximation to equilibrium freezing was not realized or that the crystals could not be properly drained. The head fraction had an estimated purity of 99.998 mole percent.

A different method of fractional freezing (method 2), used by R. S. Jessup, of the Heat Measurements Section, was more successful. He lowered a glass tube containing the molten material (39e) very slowly from a heating coil. Freezing began at the bottom of the cell and progressed upward until the whole mass was frozen. The portion remaining liquid was stirred constantly. About 50 grams was frozen in 6 hours. The glass tube was cut so that the last portion of the solid to freeze (one-third to one-fourth) was discarded. The process was then repeated with the remainder. Purification by this method was more effective than by the first method of fractional freezing. The purity of the best preparation exceeded 99.999 percent. The substance was allowed to freeze very slowly and nearly ideal conditions for separation were evidently obtained.

(c) CRYSTALLIZATION FROM SOLVENTS

In recrystallizing benzoic acid from solvents, ethyl alcohol, which is sometimes recommended for this purpose, was found unsuitable because ethyl benzoate is readily formed. Water and benzene are satisfactory, with a slight apparent advantage in favor of the benzene in the rate of purification by successive batch recrystallizations. The benzene was carefully purified by distillation in a highly efficient rectifying column. In each case the solvent was saturated with benzoic acid at about 100°C , the solution cooled in the usual way to about 15°C , and the recrystallized acid separated on a fritted

glass funnel. One hundred grams of a saturated aqueous solution contains 0.25 g of benzoic acid at 15° C and 5.9 g at 100° C; 100 g of a saturated solution in benzene contains about 7 g of benzoic acid at 15° C and about 78 g at 100° C.¹¹

Benzene is a more convenient solvent but not as readily available in high purity as water. The results in table 2 show that purification under the conditions which were maintained in these experiments was more efficient from benzene than from water.

After favorable experience with batch recrystallization, an apparatus was built for continuous recrystallization combined with extraction.¹² The apparatus, shown in figure 1, was essentially an elongated U-tube occupying the full height of the laboratory (about 10 feet), with a condenser connecting the upper ends of the two arms. An enlarged part near the bottom of the larger arm of the U served as a container for the solid benzoic acid. A fritted glass disk, sealed in place near the bottom of this container, supported the crystals. The funnel-shaped part of the apparatus below the disk was designed to minimize channeling. The solvent (benzene was used in the work here described) was introduced by suction into the small arm through the solvent inlet and circulated by gravity. The solvent was saturated at room temperature by dissolving benzoic acid from the bottom of the crystalline mass supported on the fritted disk. Light tapping caused the remainder of the crystalline mass to settle as this process went on. Solvent was added until the saturated solution reached the desired level in the boiler. The liquid level in the two arms was not the same because of the difference in density of pure solvent and saturated solution; however, the arms above the boiler were long enough to compensate for this difference. An electric heating element served to warm the boiler, from which nearly pure solvent distilled through a water-cooled condenser into the opposite arm of the apparatus. Evaporation was allowed to proceed at a regular rate while crystals separated in or just below the boiler. The crystals fell slowly through about 180 cm of the saturated solution and settled on the mass of solid already retained on the fritted disk. During this process the crystals were purified by washing and exchange (reaction) in a solution that was less concentrated with respect to the more soluble fraction than the solution in the boiler from which they separated. An inlet near the top of the container for the solid permitted the passage of a slow current of air up through the extractor arm, which was necessary to keep the crystals agitated and to prevent clogging. The air was saturated with benzene at room temperature to prevent loss of solvent by evaporation. When the apparatus was operated at atmospheric pressure, satisfactory separation of crystals did not occur. It was found by trial to operate properly under a pressure of 215 mm. A receiver was connected with the boiler by a tube which was fitted to the extractor arm through a ground joint. Each time after the entire charge of benzoic acid had been dissolved and recrystallized in the apparatus (at the end of each cycle), a portion of solution was removed from the boiler; and thus a

¹¹ Atherton Seidell, *Solubilities of Inorganic and Organic Compounds*, ed. 2, p. 133-135 (D. Van Nostrand Co., New York, N. Y., 1919).

¹² F. W. Rose, Jr., of the American Petroleum Institute Project 6 at the National Bureau of Standards, made many helpful suggestions in the design and application of this method, which is an adaptation to solid material of the Fenske reflux extractor. (M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem.* **28**, 1035 (1936).

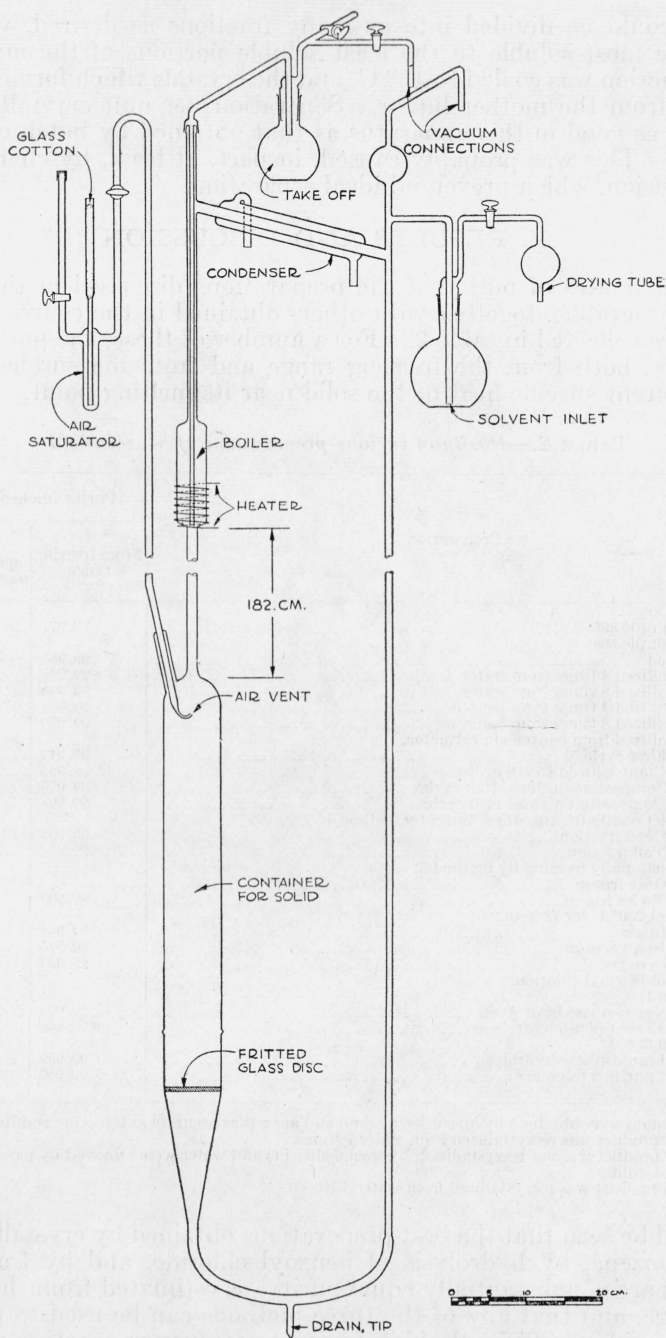


FIGURE 1.—Apparatus for continuous recrystallization.

charge could be divided into as many fractions as desired, varying from the most soluble to the least soluble portions of the material. Each fraction was cooled to 15° C, and the crystals which formed were filtered from the mother liquor. Separation per unit crystallization was not as good in this apparatus as that obtained by batch crystallization. This was probably caused, in part, at least, by channeling and diffusion, which prevented ideal separation.

V. RESULTS AND DISCUSSION

The estimates of purity of the preparations discussed in the foregoing paragraphs, together with others obtained in the course of this work, are collected in table 2. For a number of these, the purity was estimated both from the freezing range and from measurements of the apparent specific heat of the solid near its melting point.

TABLE 2.—*Purity of various preparations of benzoic acid*

Preparation	Purity (mole percent)	
	From freezing range	From specific-heat measurements
Standard Sample 39f.....	99.977	-----
Standard Sample 39e:		
Untreated.....	99.983	99.989 ₈
Recrystallized 4 times from water.....	^a 99.99 ₀	-----
Recrystallized 8 times from water.....	99.995	-----
Recrystallized 4 times from benzene.....	^a 99.99 ₂	-----
Recrystallized 8 times from benzene.....	99.999	99.999 ₃
Recrystallized from benzene in extractor:		
(a) First cycle.....	99.942	-----
(b) Composite 3d to 8th cycles.....	99.995	-----
(c) Composite 9th, 10th, 11th cycles.....	99.996	-----
(d) Composite 13th and 14th cycles.....	99.998	-----
After fractionally freezing three times by method 1:		
(a) Head fraction.....	99.998	99.995 ₃
(b) Tail fraction.....	^a 99.95 ₀	-----
After fractionally freezing by method 2:		
(a) Once frozen.....	-----	99.998 ₈
(b) Twice frozen.....	99.999	99.999 ₁
Heated at 200° C for 72 hours:		
(a) In air.....	99.954	-----
(b) In a vacuum.....	99.976	-----
(c) In oxygen.....	99.953	-----
Hydrolysis of benzoyl chloride:		
Fraction 1: ^b		
(a) Vapor-phase hydrolysis.....	99.996	-----
(b) Liquid-phase hydrolysis.....	^a 99.99 ₆	-----
Fraction 2: ^c		
(a) Liquid-phase hydrolysis.....	99.999	-----
Oxidation of purified toluene ^d	99.980	-----

^a These values were obtained by an earlier method and are not as accurate as the other results.

^b Original product was recrystallized from water 7 times.

^c Original product was not recrystallized; hydrogen chloride and water were removed by passing dry air through the liquid.

^d Original product was recrystallized from water 4 times.

It will be seen that the best preparations obtained by crystallization from benzene, by hydrolysis of benzoyl chloride, and by fractional freezing are of substantially equal purity, as estimated from the freezing range, and that any of the three methods can be used to prepare benzoic acid of sufficiently high purity to meet very exacting requirements. In using the substance two circumstances must always be

taken into account. One is that it is notably hygroscopic in the liquid phase and the other that formation of anhydride occurs, very slowly, at temperatures near the melting point of the acid if the atmosphere in contact with it is very dry (much drier than is ever encountered without intentional and thorough drying).

A valid objection may be raised to the use of the freezing (or melting) behavior as a criterion of purity for a substance purified by fractional freezing. Quite apart from the fact that the freezing range of the substance purified by fractional freezing was substantially equal to those of the best preparations obtained by crystallization from benzene and by hydrolysis of benzoyl chloride, the temperature at any given stage of freezing was identical for the three preparations, within the reproducibility of the measurements (about 0.002°C).¹³ This is independent evidence that these three preparations were identical in composition, and hence were pure substances rather than mixtures of the rare type that has a constant freezing point.

A brief comment on the freezing point of benzoic acid may be desirable. Estimation of purity from the freezing range is based entirely on sufficiently precise measurement of *differences* in temperature, rather than on any exact knowledge of the actual temperatures of freezing. Since the freezing point of benzoic acid was not of direct interest in the work reported in this paper, the resistance thermometer and bridge were not kept under calibration in a manner to permit recording absolute freezing temperatures to 0.001°C , although differences in temperature of about 0.0001°C during freezing were regarded as significant. Further, the measurement of a freezing range involves the withdrawal of heat at a rate rapid enough to cause the observed temperature to differ somewhat from the true temperature of equilibrium between the liquid and solid phases. These considerations limit the accuracy with which the freezing point of benzoic acid can be reported on the basis of the work with which this paper is concerned. The value tentatively assigned is $122.36 \pm 0.01^{\circ}\text{C}$.

WASHINGTON, September 27, 1940.

¹³ The average deviation was 0.002°C and the range was 0.005°C . The freezing temperature of the product obtained by fractional freezing fell between that of the other two.